

PATENT SPECIFICATION

(11) 1429 373

1429 373

- (21) Application No. 30297/73 (22) Filed 26 June 1973
 (31) Convention Application No. 1858/72 (32) Filed 29 Jan. 1972 in (19)
 (33) Finland (SF)
 (44) Complete Specification published 24 March 1976
 (51) INT CL² D06P 3/60
 (52) Index at acceptance
 D1B 2D
 (72) Inventors JAAKKO EINARI LAINE and
 EERO VILHELM SJÖSTRÖM



(54) A METHOD OF FIXING METAL-SPECIFIC INDICATOR GROUPS TO CELLULOSIC SUBSTRATES

(71) We, ORION-YHTYMÄ-OY, of Nilsinkatu 10—14, 00510 Helsinki 51, Finland, a Finnish Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In analytical chemistry it is desirable to develop methods for conveniently effecting both qualitative and quantitative determinations on samples converted into a liquid form.

The present invention concerns a method for fixing metal-specific indicator groups to cellulosic substrates.

In order to achieve the substantial advantages presented later on, it is advisable to fix the indicating group to the carrier substance by a chemical bond. The idea of such bonding is not new in itself: bonding has been applied, for instance, by the company Merck AG in pH indicator papers manufactured by them (German Patent No. 1 698 247). On the other hand, heretofore no metal-specific indicator groups have been fixed by means of a chemical bond. The most recent procedure within this sector is presented in a patent disclosing the adsorbing of metal-specific indicator groups into a fibrous material, which is then covered with a thin plastic film, leaving one of the margins open so that the metal solution to be examined may penetrate into the fibrous material under effect of capillary forces (Merck AG, German Patent No. 1 940 964).

Indicator groups belonging to the azo dyestuffs are particularly interesting: in the first place owing to the ease with which they can be synthesized, and secondly owing to the powerful bathochromic shift occurring in association with chelate formation in the wavelength range visible at their absorption maximum, whereby visual observations are facilitated.

According to the invention there is employed a method of fixing a metal-specific indicator group to a cellulosic substrate,

wherein azo dyestuffs which contain at least two hydroxyl groups are used as the metal-specific indicator group and *s* - triazine compound is used to link one of the hydroxyl groups of the dyestuff to the cellulosic substrate, the *s* - triazine compound becoming bonded to one of the two hydroxyl groups of the azo dyestuffs whereas the other one of the two hydroxyl groups remains available for chelate formation, characterised in that the method comprises the steps of:—

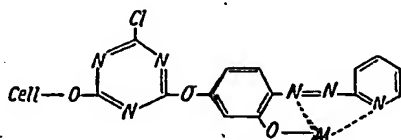
1) joining to the cellulosic substrate (A) a bridge-forming group (B) by placing the substrate (A) in a solution of borate buffer and acetone, adding an *s* - triazine compound to the said solution, washing the substrate first with water and then with acetone to produce substrate (A) plus bridge-forming group (B) as intermediate compound (A→B);

2) adjusting the pH value of the said intermediate compound (A→B) to pH 8 to produce adjusted intermediate compound (A→B)_(pH 8);

3) adding to the said adjusted intermediate compound (A→B)_(pH 8) an aqueous PAR solution to fix to the said compound a metal-specific indicator group (C) to produce end compound (A→B→C) i.e. substrate (A) plus bridge-forming group (B) plus indicator group (C);

4) recovering and washing the end compound (A→B→C).

The azo dyestuff known as PAR, or 4 - (2 - pyridylazo) resorcinol, contains a resorcinol ring, of whose two hydroxyl groups the covalent bond may be directed to that one which does not participate in the chelate formation. The bonding configuration that has been employed between cellulose and PAR is *s* - triazine derived from trifunctional cyanuric chloride. It is thus understood that the product has the structure seen in the formula reproduced below. The structure has been elicited, employing mass spectrometry and infra-red techniques among others. In the formula also a chelate structure has been suggested.



Cell is cellulose M is a metal atom

In this formula, the metal indicator group has been chemically bonded to cellulose fibre via the *s*-triazine group.

In the literature the synthesizing of numerous derivatives of phenols and cyanuric chloride have been reported, and certain phenols have in fact even been bonded to cellulose fibre by this method. It is in fact significant in the present invention that the specific indicator has been fixed by the aid of a substituent which is not essential when indicating metals.

The product thus obtained is somewhat unstable in chemical treatments. However, when in the structure of the preceding formula the chlorine in the *s*-triazine ring is replaced the product obtained may be virtually stable.

It has been found that when considerable PAR concentrations are desired in the carrier substance, certain tertiary amines act as efficient catalysts of the attachment.

The carrier substance is most appropriately cellulose or wood substance. The carrier itself may be a strip, for instance a paper strip, but it may also be present in the form of a powder or of a membrane or gel. The carrier may also be employed in columns and in batch operation. The carrier may be applied in similar uses as those products in which the indicating group has been adsorbed to the carrier substance. However, a carrier substance provided with metal indicator according to the invention has the following advantages over those mentioned above:

- (1) Feasibility of quantitative determinations;
- (2) It is possible to prepare material suitable for chromatography of metals;
- (3) The observation of particularly low metal concentrations is allowed by enriching the ions in the product; and
- (4) When ground to powder, the material may be used, for instance, in complexometric titrations and in observing the course of reactions involving changes of the degree of oxidation of metals (e.g. autooxidations catalyzed or inhibited by metal ions). It is possible to remove the powder by filtering on conclusion of the test, whereby the

products obtained may be examined free of the indicator.

Examples of the method according to the invention are presented.

Example 1

Cellulose fibres containing indicator were prepared in two stages. First, activation of the carrier substance with 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) was carried out. The indicator was attached at the following stage. The fibre to be activated (in the amount of 10 g), which in this particular instance consisted of soluble cellulose (degree of beating 17.0°SR), but which may be fibre from any process, was present in a solution composed of borate buffer (0.25 M, 200 ml) and acetone (360 ml) (at pH 12) and was cooled to -12°C. 6 g of cyanuric chloride in 100 ml acetone were added. The pH of the reaction was kept constant by adding 1-N sodium hydroxide. Ten minutes after the addition of cyanuric chloride, the fibres were washed with 4000 ml of distilled water, followed by acetone (800 ml) and finally suspended in acetone (500 ml) for a period of two hours, once more washed with acetone (400 ml) and dried in vacuum at room temperature. The suspension formed by the fibres (2 g) thus prepared and by an aqueous PAR solution (150 mg PAR in 75 ml of ion-exchanged water) was agitated for 60 minutes at room temperature. The pH of the suspension was maintained constant (at pH 8.0) by adding 1-N sodium hydroxide. On concluded reaction, the fibres were recovered by passing the suspension through a Büchner funnel, and the fibres were washed with ion-exchanged water until the washing fluid was colourless. The result is shown in Table 1.

TABLE 1
Analysis revealing association of indicator group

Degree of beating (°SR)	<i>s</i> -triazine (mmole per 100 g fibre)	PAR (mmole per 100 g fibre)	
17.0	0.7	3.6	100

Example 2

For comparison, the experiments of Example 1 were repeated, with the difference that the initial substance used consisted of soluble cellulose passed through a Valley grinder according to the SCAN Standard C25:67 to present different degrees of beating. As can be seen from Table 2, the quantity of PAR fixed increases with increasing degree of beating.

TABLE 2

Effect of beating on quantities of s-triazine and indicator fixed

	s-triazine (mmole per 100 g fibre)	PAR (mmole per 100 g fibre)
5 Degree of beating (°SR)		
17.0	8.7	3.6
23.4	10.9	4.5
36.2	17.0	7.0
10 46.0	18.5	7.6
53.6	20.7	8.5
76.4	27.9	11.5
84.0	22.8	9.4

Hydrolysis period (hrs)	Percentage of initial PAR quantity detached				
	A	B	C	D	E
0.5	5.2	0.9	1.5	2.7	0.8
4.0	6.4	1.4	2.6	5.8	3.9
68.0	20.4	1.8	2.7	9.2	7.1
92.0	22.7	1.9	3.0	9.5	8.2
140.0	27.8	2.9	3.5	10.5	8.6

It is observed from Table 4 that on treatment of a metal indicator paper product prepared by a method according to the invention with amine a stabilizing effect is obtained. This effect is strongest with aniline.

Example 3

- 15 Beaten soluble cellulose (84.0°SR) treated as in Example 1, in a quantity of 2.1 g and containing 21 mg PAR per g of fibre, was eluted in a column tube at different pH values in order to clarify its stability. The results are shown in Table 3.

TABLE 3

Stability of fibre containing metal indicator 120 ml of eluted fluid at each point

	pH	PAR in eluted fluid (mg)
25	4.0	0.34
	5.7	0.34
	7.0	0.36
	9.0	0.44
30	10.4	1.36
	11.2	1.64
	12.0	7.81

Example 4

- 35 Fibre material (10 g) beaten in a hollander engine (84.0°SR) and treated as in Example 1 was allowed to react with certain amines. 5 ml of each amine were solved in ion-exchanged water (375 ml), to which the fibres were added. The fibres were collected after 40 30 minutes in a Büchner funnel, washed with ion-exchanged water and with methanol and once more with ion-exchanged water.

- The amine-treated products obtained were hydrolyzed in buffer (pH 2), from which 45 samples were taken at given intervals for spectrophotometric determination of detached PAR. The results were compared with those of untreated fibre. The results are shown in Table 4.

TABLE 4

Effect of amine treatment on stability of product

Amines employed:	
55 Aniline	B
Piperidine	C
Ethylene diamine	D
Ammonia	E
Untreated product	A

Example 5

It is well-known that tertiary amines are better so-called departing groups in nucleophilic SN₂ reactions than chlorine. By substituting a tertiary amine for the chlorine atom in the structure formula the quantity of PAR fixed may be increased. However, the possibility of stabilizing the s-triazine ring is lost at the same time.

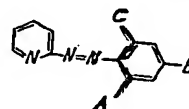
At preparation according to Example 1 of fibres containing PAR, at the associating stage of the metal indicator a tertiary amine, 1,4-diaza(2,2,2)bicyclooctane (DABCO) was added in a quantity giving a concentration of 3 g/l in the reaction mixture. In other parts the reaction was carried out as in Example 1.

Using tertiary amine as a catalyst, PAR concentrations even up to 34 mg per g fibre have been achieved.

Example 6

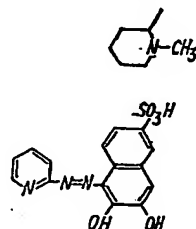
Other metal indicator groups which have been fixed according to the principle of the present invention are presented.

Pyridine analogues



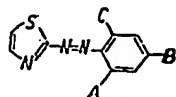
	A	B	C
5-methyl-4-(2-pyridylazo)-resorcinol	OH	OH	CH ₃
4-(3-N-methylpiperidyl-2-pyridylazo)resorcinol	OH	OH	H

which latter furthermore contains in position 3 of the pyridine ring the following group:



1 - (2 - pyridylazo) - 2,3 - dihydroxy-naphthalene - 6 - sulphonic acid

Thiazole analogues



5		A	B	C
	4-(2-thiazolylazo)resorcinol	OH	OH	H
	5-methyl-4-(2-thiazolylazo)-resorcinol	OH	OH	CH ₃

WHAT WE CLAIM IS:—

- 10 1. A method of fixing a metal-specific indicator group to a cellulosic substrate, wherein azo dyestuffs which contain at least two hydroxyl groups are used as the metal-specific indicator group and *s* - triazine compound is used to link one of the hydroxyl groups of the dyestuff to the cellulosic substrate, the *s* - triazine compound becoming bonded to one of the two hydroxyl groups of the azo dyestuffs whereas the other one of the two hydroxyl groups remains available for chelate formation, characterised in that the method comprises the steps of:—

- 25 1) joining to the cellulosic substrate (A) a bridge-forming group (B) by placing the substrate (A) in a solution of borate buffer and acetone, adding an *s* - triazine compound to the said solution, washing the substrate first with water and then with acetone to produce substrate (A) plus bridge-forming group (B) as intermediate compound (A→B);

- 30 2) adjusting the pH value of the said intermediate compound (A→B) to pH 8 to produce adjusted intermediate compound (A→B)_(pH 8);

- 35 3) adding to the said adjusted intermediate compound (A→B)_(pH 8) an aqueous PAR solution to fix to the said compound a metal-specific indicator group (C) to produce end compound (A→B→C) i.e. substrate (A) plus bridge-forming group (B) plus indicator group (C);

- 40 4) recovering and washing the end compound (A→B→C).

- 45 2. A method according to Claim 1, wherein the said steps are effected by:—

- a) placing the cellulosic substrate in said solution composed of borate buffer and acetone at pH 12,

- b) cooling the said solution to -12°C ,
 c) adding to the said solution the said *s* - triazine compound (for example solution of cyanuric chloride in acetone) while keeping the pH constant by adding 1-N sodium hydroxide,
 d) after a lapse of time washing the substrate with distilled water,
 e) washing the substrate with acetone,
 f) suspending the substrate in acetone for a period,
 g) washing the substrate with acetone,
 h) drying the substrate *in vacuo*,
 i) adjusting the pH value of the substrate to pH 8 while preparing a suspension of the substrate in an aqueous PAR solution,
 j) agitating this suspension for a period at room temperature while maintaining a constant pH 8.0 by adding 1-N sodium hydroxide, and
 k) recovering the substrate with indicator group fixed thereto and washing the same with ion-exchanged water until the washing fluid is colourless.

3. A method according to Claim 1 or 2, wherein cellulosic fibres are used as the substrate.

4. A method according to Claim 1, 2 or 3, wherein cyanuric chloride is used as an *s* - triazine compound.

5. A method according to Claim 1, 2, 3 or 4, wherein the chlorine in the *s* - triazine ring between the cellulose substrate and the azo dyestuff is replaced by nucleophil stabilizing agents.

6. A method according to Claim 5, wherein amines are used as the stabilizing agents.

7. A method according to Claim 6, wherein aniline, piperidine, ethylene diamine or ammonia are used as the amines.

8. A method according to any one of the preceding Claims, wherein the azo dyestuffs contain a pyridyl or a thiazolyl residue.

9. A method according to Claim 1 or 2, substantially as hereinbefore described.

10. A method according to Claim 1 or 2, effected in accordance with any of the Examples hereinbefore.

11. A product resulting from a method according to any of the Claims hereinbefore.

HANS & DANIELSSON,
 Chartered Patent Agents,
 32, Lodge Lane,
 London, N.12. 8JJ.

Printed for Her Majesty's Stationary Office, by the Courier Press, Leamington Spa, 1976.
 Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

BEST AVAILABLE COPY